

PATENT SPECIFICATION

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(54) A PROCESS FOR THE PREPARATION OF 2-AMINO-BENZO-THIAZOLES AND NEW PRODUCTS PREPARED THEREBY

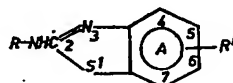
(71) We, SOCIETE NATIONALE DES PETROLES D'AQUITAINE, a French body corporate, of Tour Aquitaine, 92-Courbevoie, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns a new process for preparing 2-aminobenzothiazoles, the amine group of which is substituted. It also concerns the new products prepared by means of this process.

The aminobenzothiazoles are heterocyclic compounds having a benzene nucleus bound to the thiazole ring and having on the carbon atom in position 2 an amine group which is substituted. The benzene nucleus may also be substituted.

The aminobenzothiazoles are useful substances in industry. These compounds are powerful bactericides; for example they are particularly useful in fighting tuberculosis. They are also useful as local anaesthetics. Certain aminobenzothiazoles are used as additives in photographic emulsions; other aminobenzothiazoles are used as stabilizers for fats, paraffins, and rubbers; still others are useful as fungicides.

The products according to the invention can be expressed by the formula:



in which R can be an aryl, aralkyl, aroyl or alkaryl group. R may, for example, be phenyl, naphthyl or benzoyl and can contain electropositive or electronegative substituents such as, for example, alkyl groups, including methyl and ethyl, alkoxy groups including methoxy and ethoxy, acetoxy, hydroxy, or amino groups, halogen atoms such as chlorine, nitro or sulpho groups, alkylthio groups such as methylthio or ethylthio, and amide groups. R can also be a benzothiazolylaminophenyl group.

R' represents the optional presence of one or more substituents in the benzene nucleus A of the benzothiazole. It may be an electronegative substituent such as halogen, notably chlorine, or an alkyl or alkoxy group.

According to one feature of the invention there is provided a 2-aminobenzothiazole substituted at the amino group by a halogenophenyl, alkoxyphenyl, alkoxybenzoyl, halogenobenzoyl, acetoxybenzoyl, alkylthiobenzoyl, a nitrobenzoyl radical, a methylthiophenyl, a naphthyl or a benzothiazolylamino radical, or at the amino group and on the benzene ring by a phenyl radical and a halogen respectively, a benzoyl radical and a halogen respectively, or a chlorobenzoyl radical and a halogen respectively.

It has already been stated in a previous publication that 2-aminobenzothiazole may be obtained by a condensation reaction between phenyl isocyanate and *ortho*-aminothiophenol (Beilstein Handbuch des Organischen Chemie 1887, page 1796).

[Price 25p]

Since then, it appears that no further work has been carried out on this subject. This situation doubtless stems from the difficulty of obtaining this product, and from the particular difficulty of obtaining its derivatives by this method. In fact, if this condensation is carried out simply by placing the reactants in contact with one another, the reaction is self-catalyzing and becomes extremely violent and hard to control, especially with respect to preventing the formation of disulphides. Furthermore, it is apparently impossible to perform this condensation and obtain the corresponding aminobenzothiazole when the benzene nucleus joined to the *ortho*-aminothiophenol is substituted by an R' substituent as defined above. These *ortho*-aminothiophenols are extremely unstable compounds, and as soon as they form they are transformed into disulphides. The process described by Beilstein in 1887 therefore does not make it possible to obtain easily certain substituted aminobenzothiazoles—up till now unknown—from isothiocyanates and aminothiophenols.

On the basis of the known prior art, it is possible to prepare aminobenzothiazoles by the oxidation of the arylthiourea. However, this method requires starting materials that are hard to obtain. Furthermore, it is not possible to obtain all the substituted aminobenzothiazoles by the action of an acid chloride on 2-aminobenzothiazole. This process is unsuitable because the starting materials contain already-formed thiazole rings, so that it is possible to obtain only a very limited number of compounds.

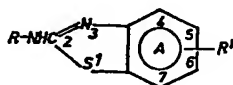
The present invention overcomes some of the problems and provides a relatively simple process which can be carried out industrially to give good yields; it largely prevents the formation of disulphides, enables an economically worthwhile manufacturing process using readily available ingredients to be carried out, and it further makes possible the preparation of a whole range of new products that could not be obtained with the above-mentioned earlier known processes.

The process according to the present invention consists in the reaction of an organic isothiocyanate with an aminothiophenol or, preferably, with a strong acid addition salt thereof, in particular with its hydrochloride, in the presence of a suitable solvent. Organic isothiocyanates correspond to the formula $R-N=C=S$, where R represents the same groups as above. Diisothiocyanates having the formula

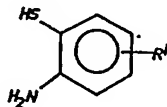


may also be used, where R'' is a divalent group corresponding to R, with one fewer hydrogen atom.

According to the invention we provide a process for preparing 2-aminobenzothiazoles having the general formula:



in which R' is H or one or more substituents, and R is an aryl, aralkyl, aroyl or alkaryl group, by the reaction between an isothiocyanate $R-N=C=S$ or di-isothiocyanate $S=C=N-R''-N=C=S$, in which R'' is as defined above and a 2-aminothiophenol having the formula:



or an acid addition salt thereof, in a non-acidic solvent which is inert to the products and starting materials and to H_2S , which is capable of dissolving the starting materials and which has a boiling point higher than the temperature at which the reaction occurs. The process can thus be performed with phenyl-, methyl- or dimethyl-phenyl-, ethyl- or diethylphenyl-, butylphenyl-, methoxyphenyl-, acetoxyphenyl-, hydroxyphenyl-, chlorophenyl-, benzoyl-, chlorobenzoyl-, methoxy-, acetoxybenzoyl-, methylthiobenzoyl-, nitrobenzoyl-, methylthiophenyl- or naphthyl-isothiocyanates or *p*-(bis-isothiocyanato) benzene.

The process can be carried out with aminothiophenols such as 2-aminothiophenol, 4-chloro 2-amino-thiophenol, and 3-methoxy-2-amino-thiophenol, this list being non-limitative.

The presence of a solvent in the reactive medium is of primary importance in the obtaining of pure aminobenzothiazoles with a good yield.

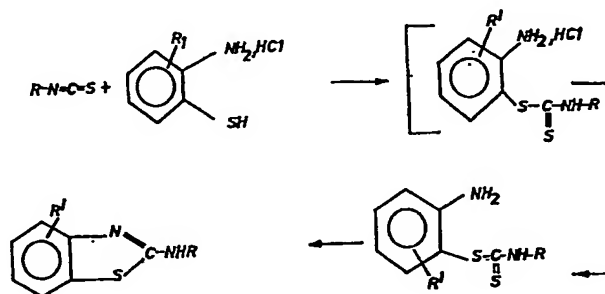
The aminothiophenols are largely unstable substances, and readily oxidize into disulphides. The solvent considerably reduces the violence of the reaction so that two molecules of *ortho*-aminothiophenol no longer condense together, there occurring instead a milder reaction between the *ortho*-aminothiophenol and the isothiocyanate, the formation of disulphides thereby being prevented to a great extent. The solvent used must possess certain properties; it must be capable of dissolving the starting materials, stable in the presence of H₂S which is released during the reaction, and inert with respect to the starting materials and end product. In addition, its boiling point must be higher than the temperature at which the reaction occurs. The reaction according to the invention may take place at temperatures ranging from 0° to 200° C. or 250° C.; preferably between 30° C. and 160° C. Higher temperatures are recommended (generally in the 80° to 200° C. range and preferably 100–150° C.) when the aminothiophenol is in the free state. On the other hand, lower temperatures, generally in the 0° C. to 80° C. range, are used when the aminothiophenol is in the form of a strong acid addition salt, particularly in the form of the hydrochloride. It is also preferable, although not indispensable, for the solvent used not to be capable of dissolving a significant proportion of the 2-aminobenzothiazole product, for example at low temperatures, this makes it possible to purify the aminobenzothiazole by means of successive crystallizations in this solvent. The solvents can be selected from an extremely wide range of substances (for example amides, aryl hydrocarbons, or mixtures of such hydrocarbons) provided they possess the properties listed above. When the basic ingredients include a phenylisothiocyanate or a substituted phenyl-isothiocyanate and an *ortho*-aminothiophenol, good results are obtained by using hydrocarbon solvents, for example toluene, mesitylene or xylene, or other solvents, for example hexamethylphosphotriamide, dimethylacetamide, or dimethylformamide.

It has thus been possible to obtain, under careful operating conditions, with a controlled reaction, aminobenzothiazoles corresponding to the condensation of phenyl-, *para*-chlorophenyl-, *ortho*- or *para*-methoxyphenyl-, *ortho*-hydroxyphenyl-, benzoyl-, *para*-chlorobenzoyl-, *para*-methoxy- or *ortho*-, *meta*- or *para*-acetoxybenzoyl-, *ortho*-, *meta*-, or *para*-methylthiobenzoyl- or *para*-nitrobenzoylisothiocyanate with *ortho*-aminothiophenol, using xylene as a solvent for the reactive medium. In these cases the reaction occurs at about 140° C. The aminobenzothiazole, which is not soluble in xylene, crystallizes directly in the reactive medium on cooling. The aminobenzothiazole is obtained with a yield of 70% to 80%, the remainder being disulphide.

If the reaction is carried out in the absence of a solvent, the benzothiazole yield amounts to only 40% to 50%, the proportion of disulphide being much greater. If a completely pure product is required, it is recrystallized in a suitable solvent, as indicated in Tables I, II and III.

When the aminobenzothiazole to be prepared includes an R' substitution of the A nucleus, the basic starting material is a substituted aminothiophenol and is an extremely unstable compound. These compounds readily oxidize into disulphides, and the reaction between a free substituted aminothiophenol and the isothiocyanate is very limited. According to the present invention, it has been found that it is better to start with an aminothiophenol salt, and particularly with a hydrochloride, the latter completely preventing the formation of disulphides. The aminothiophenol is no longer involved in the reaction in the form of a free base and since the amine function is blocked, the oxidation reaction can no longer take place. In this case, the solvent used must possess the properties listed above, but it must also play a role in the reactive medium; it must have basic characteristics that will trigger the release of the hydrochloric acid when the thiol function has already reacted with the isothiocyanate, and then make the benzothiazole cyclization possible.

The reaction in this case may be considered as being as follows:



In the case of free *ortho*-aminothiophenol, its hydrochloride can also be used as the starting material. The aminobenzothiazole yield is equally as good as when the reaction is started with *ortho*-aminophenol; in this case, therefore, it is not necessary to start with aminothiophenol hydrochloride.

The basic solvents suitable for achieving the condensation of an aminothiophenol hydrochloride with an isothiocyanate must be highly polar solvents, since they must be solvents for hydrogen chloride. The most suitable compounds having basic properties are amides. The following are examples of suitable amides; hexamethylphosphotriamide, dimethylacetamide, and dimethylformamide. When the aminothiophenol hydrochloride is used as the starting product, the reaction should occur between 40° C. and 50° C. The hydrochloride is stable in these solvents, and the amine is released after an initial addition of isothiocyanate onto the —SH group. In this case, the products obtained are soluble in the reactive medium; they readily crystallize by precipitation in water, and for purification purposes they can be recrystallized in a suitable solvent.

The reaction is generally carried out with a stoichiometric proportion of isothiocyanate and aminothiophenol. When a diisothiocyanate is used instead of a monoisothiocyanate, the proportion of reactants should be 2 moles of aminothiophenol for 1 mole of diisothiocyanate.

The amount of solvent used for dissolving the reactive ingredients can vary. As a rule, 1 or 2 moles of isothiocyanate are dissolved in one litre of solvent; when the dissolution is complete, a solution of 1 to 2 moles of aminothiophenol in one litre of solvent is added.

The examples below illustrate the invention. They show the results obtained according to different embodiments of the process.

Examples 1 to 3.

Reaction of *ortho*-aminothiophenol with an isothiocyanate in the absence of a solvent.

A quantity of 2-*ortho*-aminothiophenol is mixed with an equimolecular quantity of an isothiocyanate (phenyl isothiocyanate in example 1, *ortho*-tolyl isothiocyanate in example 2, and benzoyl isothiocyanate in example 3). Within a few minutes an extremely violent exothermic reaction begins accompanied by an abundant emission of H₂S. When the reaction is brought under control the reactive medium is maintained in a water bath at 100° C. for as long as the H₂S continues to be released. The crude product obtained is a solid. It is recrystallized in a suitable solvent.

The results are recorded in Table I, below.

Examples 4 to 14.

Reaction of *ortho*-aminothiophenol with an isothiocyanate in the presence of a solvent.

In a three-litre flask, 1 to 2 moles of 2-*ortho*-aminothiophenol are placed in one litre of xylene; this mixture is refluxed. To this solution is carefully added a solution of 1 to 2 moles of isothiocyanate in one litre of xylene. Reflux is maintained until the end of the gaseous emission. The reaction lasts from 30 to 60 minutes. The reactive mixture is allowed to cool. The benzothiazole crystallizes in the xylene. It is dried and recrystallized in the same solvent or in another suitable solvent.

The following isothiocyanates are used: phenyl-, *para*-chlorophenyl-, *ortho*- and *para*-methoxyphenyl-, *ortho*-hydroxyphenyl-, benzoyl-, *para*-chlorobenzoyl-, *para*-

5 methoxy- and *para*-acetoxybenzoyl-, *para*-methylthiobenzoyl-, and *para*-nitrobenzoyl-isothiocyanate. The corresponding aminobenzothiazoles are obtained. The results are recorded in Table II with respect to the benzothiazole melting point obtained; the recrystallization solvent used, and the yield obtained. It can be seen that when the isothiocyanate is the same as in examples 1 to 3, and when a solvent is used, the yield is discernibly improved. Among the aminobenzothiazoles obtained, those corresponding to examples 5, 6, 8, 9, 10, 11 and 12 are new compounds. 5

Examples 15 to 23.

10 Reaction of *ortho*-aminothiophenol hydrochloride (substituted or unsubstituted) with an isothiocyanate in the presence of an extremely polar basic solvent. 10

One to two moles of 2-*ortho*-aminothiophenol hydrochloride are dissolved in one litre of a basic solvent such as hexamethylphosphotriamide, dimethylacetamide, or dimethylformamide. To this solution is carefully added a solution of 1 to 3 moles of isothiocyanate in one litre of the same solvent. The solution is maintained at 40°—15 50° C. until the gaseous emission ends. The reactive solution is poured into a volume of water equal to ten times that of the organic solution. The benzothiazole precipitates. It is dried and recrystallized in a suitable solvent. 15

The results are recorded in Table III. From this table, it can be seen that the results are practically identical to those obtained in the examples 4 to 14, the starting material being either 2-*ortho*-aminothiophenol or its hydrochloride, but if a substituted 20 *ortho*-aminothiophenol is used, satisfactory results are obtained only if the corresponding hydrochloride is used. It is impossible to use a substituted *ortho*-aminothiophenol because of its instability, which leads to the formation of disulphides. 20

Example 24.

25 In a three-litre flask is placed 1 mole of *ortho*-aminothiophenol in one litre of xylene; this mixture is brought to reflux until it is completely dissolved. To this solution is gradually added a solution of 1 mole of *para*-methylthiophenyl-isothiocyanate in one litre of xylene. Reflux is maintained until the H₂S gaseous emission has ended, i.e. for about 60 minutes. The reactive mixture is allowed to cool. 2-(*p*-methylthio-30 phenyl-amino) benzothiazole crystallizes in the xylene. It is dried and recrystallized from benzene. Benzothiazole yield: 90%. Melting point: 170° C. 30

Example 25.

With the same procedure as in example 24, using the *ortho*-aminothiophenol dissolved in one litre of xylene and 1 mole of α -naphthyl isothiocyanate dissolved in one litre of xylene, after a 60-minute reaction, an 85% yield of 2-(α -naphthylamino)benzothiazole is obtained which, after recrystallization in benzene, has a melting point of 198° C. 35

Example 26.

40 With the same procedure as in example 24, using 2 moles of *ortho*-aminothiophenol dissolved in one litre of xylene, and 1 mole of *p*-(bis-isothiocyanato)-benzene dissolved in one litre of xylene, maintained under reflux for approximately one hour, a yield of 82% of *p*-(bis-2-aminobenzothiazolylamino) benzene is obtained which, after recrystallization in ethyl acetate and ethanol, has a melting point of 292° C. 40

Examples 24 to 26 are summarised in Table IV.

TABLE I

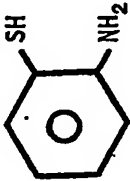
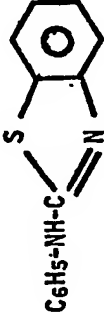
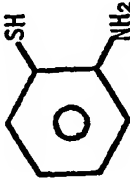

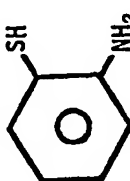
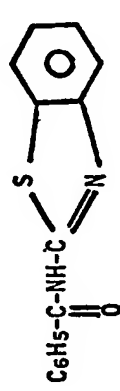
Ex. No	Amino-thiol	Isothiocyanate	Benzothiazole	MP°C	Recrystallization solvent	Yield %
1		$\text{C}_6\text{H}_5\text{-NCS}$	 $\text{C}_6\text{H}_5\text{-NH-C}\equiv\text{N}$	158	benzene	55
2		$\text{o-CH}_3\text{-C}_6\text{H}_4\text{-NCS}$	 $\text{o-CH}_3\text{-C}_6\text{H}_4\text{-NH-C}\equiv\text{N}$	124	benzene	48
3		$\text{C}_6\text{H}_5\text{-C(=O)-NCS}$	 $\text{C}_6\text{H}_5\text{-C(=O)-NH-C}\equiv\text{N}$	189 190	benzene	60

TABLE II

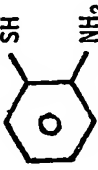
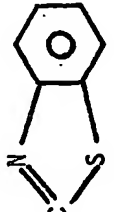
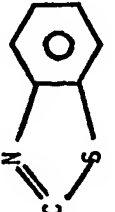
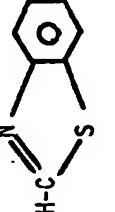

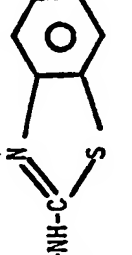
Ex. No.	Amino-thiol	Isothiocyanate	Benzothiazole	mp°C	Recrystallization solvent	Yield %
4		$\text{C}_6\text{H}_5\text{-NCS}$	 $\text{C}_6\text{H}_5\text{-NH-C}$	158	benzene	90
5	-	$p\text{-Cl-C}_6\text{H}_4\text{-NCS}$	 $p\text{-Cl-C}_6\text{H}_4\text{-NH-C}$	210	benzene	81
6	-	$p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-NCS}$	 $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-NH-C}$	160	benzene	85
7	-	 $\text{C}_6\text{H}_5\text{-C-NCS}$	 $\text{C}_6\text{H}_5\text{-C-NH-C}$	189	benzene	85

TABLE II (continuation)

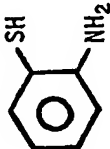
Ex. N°	Amino-thiol	Isothiocyanate	Benzothiazole	MP°C	Recrystallization solvent	Yield %
8		$p\text{-Cl-C}_6\text{H}_4\text{-C(=O)-NCS}$	$p\text{-Cl-C}_6\text{H}_4\text{-C(=O)-NH-C(=S)-S-C}_6\text{H}_5$	224	ethanol	75
9	-	$p\text{-CH}_3\text{-C(=O)-O-C}_6\text{H}_4\text{-C(=O)-NCS}$	$p\text{-CH}_3\text{-C(=O)-O-C}_6\text{H}_4\text{-C(=O)-NH-C(=S)-S-C}_6\text{H}_4\text{-N}$	213 214	ethanol	95
10	-	$p\text{-CH}_3\text{-O-C}_6\text{H}_4\text{-C(=O)-NCS}$	$p\text{-CH}_3\text{-O-C}_6\text{H}_4\text{-C(=O)-NH-C(=S)-S-C}_6\text{H}_4\text{-N}$	200 201	ethanol	87
11	-	$p\text{-CH}_3\text{-S-C}_6\text{H}_4\text{-C(=O)-NCS}$	$p\text{-CH}_3\text{-S-C}_6\text{H}_4\text{-C(=O)-NH-C(=S)-S-C}_6\text{H}_4\text{-N}$	170	ethanol	92

TABLE II (continuation)

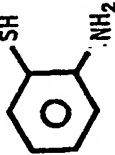
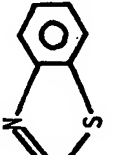
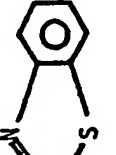

Ex. No	Amino-thiol	Isothiocyanate	Benzothiazole	MP °C	Recrystallization solvent	Yield %
12		$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-C(=O)-NCS}$	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-C(=O)-NH-C(=S)-N}$ 	298	ethanol	62
13	-	$o\text{-CH}_3\text{O-C}_6\text{H}_4\text{-NCS}$	$o\text{-CH}_3\text{O-C}_6\text{H}_4\text{-NH-C(=S)-N}$ 	152	benzene	80
14	-	$o\text{-HO-C}_6\text{H}_4\text{-NCS}$	$o\text{-HO-C}_6\text{H}_4\text{-NH-C(=S)-N}$ 	178	benzene	77

TABLE III

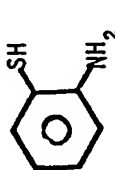
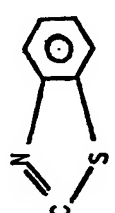
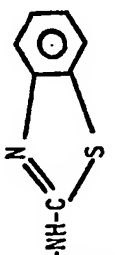
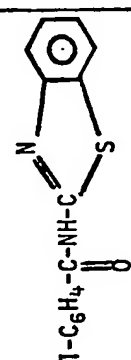
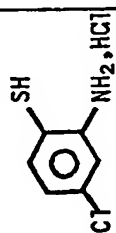
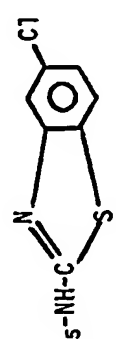
Ex. No	amino-thiol or hydrochloride	isothiocyanate	Benzothiazole	Mp°C	Recrystallization solvent	Yield %
15	 (or its hydrochloride)	$\text{C}_6\text{H}_5\text{-NCS}$	 $\text{C}_6\text{H}_5\text{-NH-C}$	158	benzene	90
16	— —	$\text{C}_6\text{H}_5\text{-C(=O)-NCS}$	 $\text{C}_6\text{H}_5\text{-C-NH-C}$	190	benzene	85
17	— —	$p\text{-Cl-C}_6\text{H}_4\text{-C(=O)-NCS}$	 $p\text{-Cl-C}_6\text{H}_4\text{-C-NH-C}$	224	ethanol	75
18	 $\text{NH}_2\cdot\text{HCl}$	$\text{C}_6\text{H}_5\text{-NCS}$	 $\text{C}_6\text{H}_5\text{-NH-C}$	230	benzene— acetone	82

TABLE III (continuation)

Ex. N°	amino-thiol hydrochloride	Isothiocyanate	Benzothiazole	mp°C	Recrystallization solvent	Yield %
19		$\text{C}_6\text{H}_5\text{-C(=O)-NCS}$		239	ethanol	90
20	— —	$p\text{-Cl-C}_6\text{H}_4\text{-C(=O)-NCS}$		285	ethanol	70
21	— —	$\text{C}_6\text{H}_5\text{-C(=O)-NCS}$		248	ethanol	85

TABLE III (continuation)

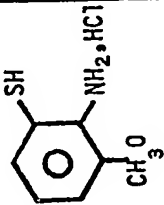

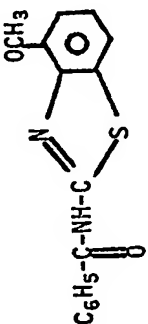
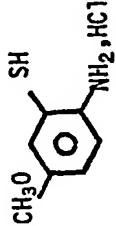


Ex. N°	amino-thiol hydrochloride	Isothiocyanate	Benzothiazole	Mp° C	Recrystallization solvent	Yield %
22				175	benzene	84
23				200	benzene	83

TABLE IV

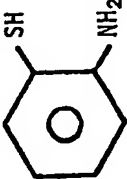
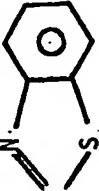
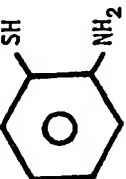
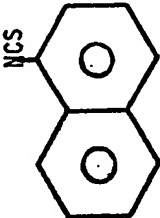
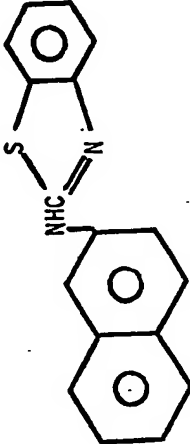
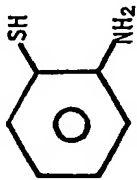

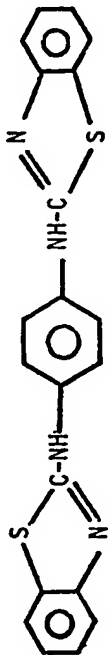
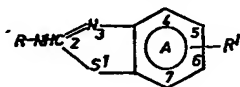
Ex. N°	Aminophénol	Isocyanate	
24		$p\text{-CH}_3\text{-SC}_6\text{H}_4\text{-NCS}$	<p></p> <p>$p\text{-CH}_3\text{-SC}_6\text{H}_4\text{-NHC}$</p> <p>Yield 90% Recrystallization solvent : benzene Melting point : 170°C</p>
25			<p></p> <p>Yield 85% Recrystallization solvent : benzene Melting point : 198°C</p>

TABLE IV (continuation)

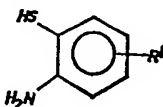
Ex. N°	Aminophenol	Isocyanate	
26			<div><p>Yield 82% Recrystallization solvent : ethanol-ethyl acetate Melting point : 292°C</p></div>

WHAT WE CLAIM IS:—

1. A process for preparing 2-aminobenzothiazoles having the general formula:



5 in which R' is hydrogen or one or more substituents and in which R is an aryl, aralkyl, 5 aroyl or alkaryl group, by the reaction between an isothiocyanate $R-N=C=S$ or diisothiocyanate $S=C=N-R''-N=C=S$, in which R is as defined above and R'' is a divalent group corresponding to R but with one fewer hydrogen atom, and a 2-aminothiophenol having the formula:



10 where R' is as defined above, or an acid addition salt thereof, in a non-acidic solvent which is inert to the products and starting materials and to H_2S , which is capable of 10 dissolving the starting materials, and which has a boiling point higher than the temperature at which the reaction occurs.

2. A process according to claim 1, wherein the solvent is an aryl hydrocarbon, a 15 mixture of such hydrocarbons, or an amide.

3. A process according to claim 1, wherein the hydrochloride of the 2-amino- 15 thiophenol is used.

4. A process according to claim 1, wherein when a salt of a 2-aminothiophenol is 20 used, the solvent is basic and polar.

5. A process according to claim 1, wherein the solvent is selected from solvents 20 in which the substituted 2-aminobenzothiazole product is insoluble or only slightly soluble.

6. A process according to claim 2, wherein the 2-aminothiophenol is in the free state 25 and the operation is carried out at a temperature of between $80^\circ C.$ and $200^\circ C.$

7. A process according to claim 1 wherein a strong acid addition salt of the 2- 25 aminothiophenol is used and the reaction is carried out at a temperature of between $0^\circ C.$ and $80^\circ C.$

8. A 2-aminobenzothiazole substituted at the amino group by a halogenophenyl 30 radical.

9. A 2-aminobenzothiazole substituted at the amino group by an alkoxyphenyl or 30 an alkoxybenzoyl radical.

10. A 2-aminobenzothiazole substituted at the amino group by a halogenobenzoyl 35 radical.

11. A 2-aminobenzothiazole substituted at the amino group by an acetoxybenzoyl 35 radical.

12. A 2-aminobenzothiazole substituted at the amino group by an alkylthio- 35 benzoyl radical.

13. A 2-aminobenzothiazole substituted at the amino group by a nitrobenzoyl 40 radical.

14. A 2-aminobenzothiazole substituted at the amino group and on the benzene 40 ring, wherein the amino group substituent is a phenyl radical and the benzene ring substituent is a halogen.

15. A 2-aminobenzothiazole substituted at the amino group and on the benzene 45 ring, wherein the amino group substituent is a benzoyl radical and the benzene ring substituent is a halogen.

16. A 2-aminobenzothiazole substituted at the amino group and on the benzene 45 ring, wherein the amino group substituent is a chlorobenzoyl radical and the benzene ring substituent is a halogen.

17. A 2-aminobenzothiazole substituted at the amino group by a methylthiophenyl 50 group.

18. A 2-aminobenzothiazole substituted at the amino group by a naphthyl group. 50

19. A 2-aminobenzothiazole substituted at the amino group by a benzothiazolyl- 55 aminophenyl group.

20. A process according to claim 4 wherein the solvent is hexamethyl phosphotri- 55 amide, dimethylacetamide, or dimethylformamide.

21. Substituted 2-aminobenzothiazoles substantially as herein described with reference to Examples 5, 6, 8, 9, 10, 11 and 12.

22. A process for preparing substituted 2-aminobenzothiazoles substantially as herein described with reference to the Examples.

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